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Thin films and multilayers of functional ceramics have a number of important applications including dielectrics, magnetic recording media, piezoelectric transducers, and integrated optical devices. Variously functionalized self-assembled monolavers, attached to single-crystal silicon substrates, were used to direct the deposition of thin films of the oxides of titanium, zinc, iron, and zirconium, at low temperatures and ambient pressures. The films were uniform, adherent, and pore-free and were, in many cases, comprised of micro-crystalline oxide particles. The monolayer functionality found to be most generally useful for these purposes included hydroxyl, carboxylate, and sulfonate functionality. In some cases the films contained desirable forms of the oxides that were different than those normally obtained: i.e., the anatase form of titania as opposed to rutile, and the tetragonal form of zirconia as opposed to monoclinic version. The patterning of the oxide films by patterning the underlying monolayer was also demonstrated. This project developed new technologies for the production of functional ceramics by creating templates for their deposition from solution and as such is a first step towards the generalized control of microstructural and crystallographic order by interface design in composite organic/inorganic materials.

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Biomimetic Fabrication of Functional Ceramic Composites Project Period: 6/1/92 - 5/30/96 AFOSR #49620-92-J-0282

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Abstract

Thin films and multilayers of functional ceramics have a number of important applications including dielectrics, magnetic recording media, piezoelectric transducers, and integrated optical devices. Variously functionalized self-assembled monolayers, attached to single-crystal silicon substrates, were used to direct the deposition of thin films of the oxides of titanium, zinc, iron, and zirconium, at low temperatures and ambient pressures. The films were uniform, adherent, and pore-free and were, in many cases, comprised of micro-crystalline oxide particles. The monolayer functionality found to be most generally useful for these purposes included hydroxyl, carboxylate, and sulfonate functionality. In some cases the films contained desirable forms of the oxides that were different than those normally obtained: i.e., the anatase form of titania as opposed to rutile; and the tetragonal form of zirconia as opposed to monoclinic version. The patterning of the oxide films by patterning the underlying monolayer was also demonstrated. This project developed new technologies for the production of functional ceramics by creating templates for their deposition from solution and as such is a first step towards the generalized control of microstructural and crystallographic order by interface design in composite organic/inorganic materials.

Patents

Mark R. DeGuire, Arthur H. Heuer, and Chaim N. Sukenik; Synthesis of Metal Oxide Thin Films U.S. Patent No 5,352,48, issued 4 October 1994. Additional continuation in part issued in 1996.

Student theses submitted to CWRU

Ph.D. theses of Rochael J. Collins (Chemistry, 1997) and Hyunjung Shin (Material Science, 1996) and M. Sc. theses of Hyunjung Shin (Material Science, 1994), Mou Maiti (Material Science, 1995) and Sitthisuntorn Supothina (Material Science, 1995).

Published scientific papers in professional journals:

- 1) "Synthesis and Characterization of TiO₂ Thin Films on Organic Self-Assembled Monolayers: I. Film Formation from Aqueous Solutions", Shin, H.; Collins, R.J.; DeGuire, M.R.; A.H.; Sukenik, C.N. *Journal of Materials Research*, 10, 692-698 (1995).
- 2) "Synthesis and Characterization of TiO₂ Thin Films on Organic Self-Assembled Monolayers: II. Film Formation via an Organometallic Route", Shin, R.; Collins, R.J.; DeGuire, M.R.; Heuer, A.H.; Sukenik, C.N. *Journal of Materials Research*, 10, 699-703 (1995).
- 3) "Sulfonate-Functionalized, Siloxane-Anchored, Self-Assembled Monolayers", Collins, R.J.; Sukenik, C.N. *Langmuir*, 11, 2322-2324 (1995).
- 4) "Deposition of Oxide Thin Films on Silicon using Organic Self-Assembled Monolayers", DeGuire, M.R.; Shin, H.; Collins, R.; Agarwal, M.; Sukenik, C.N.; Heuer, A.H. Integrated Optics and Microstructures III, M. Tabib-Azar Ed., Proc. SPIE, 2689, 88-99 (1966).
- 5) "Low Temperature Deposition of Patterned TiO₂ Thin Films Using Photopatterned Self-Assembled Monolayers", Collins, R.J.; Shin, H.; DeGuire, M.R.; Sukenik, C.N.; Heuer, A.H. Applied Physics Letters, 69, 860-862 (1996).
- 6) "Photocontrolled Formation of Hydroxyl-Bearing Monolayers and Multilayers", Collins, R.J.; Bae, I.T.; Scherson, D.A.; Sukenik, C.N. *Langmuir*, 12, 0000 (November, 1996).
- 7) "Solid-State Diffusive Amorphization in TiO₂/ZrO₂ Bilayers", Shin, H.J.; Agarwal, M.; DeGuire, M.R.; Heuer, A.H. J. Amer. Cer. Soc., 79, 1975-1978 (1996).